

PCT

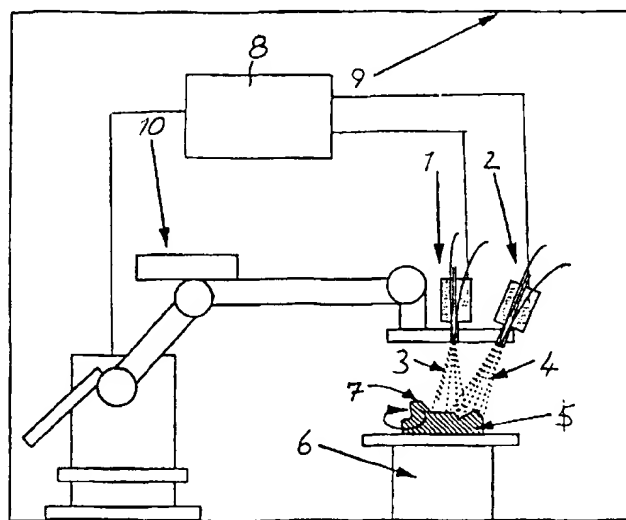
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: SPRAY DEPOSITION PROCESS



(57) Abstract

A process for producing a metallic tool, mould, die or other body of significant thickness or a coating, the process comprising directing a spray (3, 4) comprising molten metallic droplets carried by a propelling gas toward an object surface (7) of a substrate or pattern (5) so as to build up a metallic deposit or coating comprising the mould, tool, die, body or coating on the object surface (7) of the substrate or pattern (5), wherein at one or more predetermined stages during spraying droplets of a relatively large mean size are sprayed and at one or more other stages droplets or a relatively smaller mean size are sprayed.

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Spray Deposition Process

5 The present invention relates to a spray deposition process and in particular to a metallurgical spray deposition process.

10 The process is also useful for producing thick and thin coatings and other sprayed metal deposits sprayed onto substrates of all kinds, particularly where some of the topographical features are difficult to cover or fill due to complex geometries.

15 It is known to use metallurgical spray deposition techniques for producing tools, moulds, dies and other bodies of significant thickness. Problems have been encountered in using such techniques from the point of view of inherent porosity in the spray deposited material and internal stresses which arise during the spray
20 deposition processes. Attempts have been made to deal with these problems and known techniques are described in, for example, WO-A-96/09421 and PCT patent application GB97/00590.

25 In a wide variety of commercially important thermal spray processes, the manner in which sprayed droplets impinge, spread and solidify on deposition is critical in influencing the subsequent properties of the manufactured coating or deposit. The first droplets to be deposited
30 will determine the properties at the coating/substrate interface. In the case of spray forming of free standing shapes for mould tooling, the first deposited droplets determine the accuracy of replication and tooling wear

properties. As deposition continues, droplet deposition behaviour controls the bulk microstructure (such as volume fraction, morphology and size of porosity) consequently determining the coating or deposit bulk properties. At all stages of deposition, droplet rebounding or splashing leads to a reduction in process yield. Recent experimental evidence suggests that droplet splashing occurs to a significant and greater extent than previously believed.

10

A further problem with sprayforming onto patterns or substrates having an object surface of varied (three dimensional) topography arises due to the fact that metal spray processes are "line of sight" processes in which known effects of shadowing and bridging occur for certain configurations of object surface topography.

15

A further problem occurs at internal and external edges of object surface topography, where poor quality deposit integrity can occur resulting in poor quality integrity to the deposit. This can result in flaking or crumbling of the deposit at corners and edges.

20

An improved spray deposition process has now been devised. According to the invention there is provided a process for producing a metallic tool, mould, die or other body of significant thickness or a coating, the process comprising directing a spray comprising molten metallic droplets carried by a propelling gas toward an object surface of a substrate or pattern so as to build up a metallic deposit or coating comprising the mould, tool, die, body or coating on the object surface of the substrate or pattern, wherein at one or more predetermined stages during spraying droplets of a relatively large mean size are

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sprayed and at one or more other stages droplets of a relatively smaller mean size are sprayed.

5 The relatively larger droplets are preferably sprayed at a stage preceding the spraying of relatively smaller droplets. Desirably, where the substrate or pattern includes topographical relief features, the spraying of the relatively larger droplets is dependent upon the nature of and/or the location of the topographical relief
10 features.

It is a preferred feature of the invention that when spraying over portions of the object surface comprising topographical features with a depth/width aspect ratio for
15 example, or into or onto sharp corners or the like, that metallic droplets of relatively large sizes are sprayed, at least initially, in order to reduce shadowing, bridging, and poorly defined edge or corner detail which has been found to be a problem with prior art techniques.

20 It has been found that for producing detail and reducing shadowing or bridging, metallic spray droplets of mean diameters of substantially 200 microns and above (preferably substantially 350 microns and above) produce
25 highly beneficial results. This result is surprising because trends in spray deposition research and practices have herebefore tended to suggest that finely sprayed -- droplets and relatively higher droplet spray velocities should produce improved results during the manufacture of
30 coatings and most other products when using spray deposition techniques. Smaller droplet sizes have also been preferred because deposit porosity is minimised by using smaller droplet sizes. This is one of the premises behind the development of techniques such as plasma

spraying and high velocity oxy-fuel metallic spraying techniques.

5 Additionally, spraying of larger droplet sizes for initial deposition (including for coatings) has been found to result in reduced porosity in the deposited material immediately adjacent the substrate or pattern.

10 It is preferred that the propelling gas of the spray is within a pressure range lower than that normally recommended for use with a particular metal spraying apparatus. The operating pressure will therefore be different for different equipment, but is preferably at or about 3 bar or less. This results in the relatively large
15 droplets desired, and relatively low droplet velocities compared with known techniques.

20 It is preferred that the droplets are produced by arc spraying, because arc spraying typically produces coarser droplet sizes than other known spray deposition processes. Conventional arc spraying apparatus has however not been designed for spraying at the larger droplet sizes of the present invention and modification and frequent cleaning of arc spray guns during proving of the invention has been
25 found to be necessary. It is believed that this is strongly indicative of the process of spraying metallic droplets at the dimensions preferred being novel and inventive per se.

30 Preferably relatively high currents are used in the arc spraying process compared with the currents used in conventional arc spraying techniques.

It is important to control internal stresses in relatively

thick deposited bodies formed in metallurgical spray deposition processes. WO-A-96/09421 discloses metallurgical spray deposition techniques which may be used to control internal stresses in deposited bodies.

5 The relatively large droplet sizes required to improve reproduction of detail and edge definition from the object surface of the substrate or pattern (and also to inhibit bridging or shadowing) have however been found not to be suitable for control of stresses. It is therefore
10 preferred that in the process according to the invention, process parameters are varied such that the relatively larger droplets are sprayed during the period and over the areas where detail of the substrate is required to be reproduced. Relatively smaller droplets are sprayed after
15 the period when the detail has been replicated as required, and in other portions of the deposit where it is not required to replicate detail, preferably under conditions to control internal stresses in the deposit.

20 Typically therefore, the process according to the invention may comprise initial spraying of relatively large droplets onto the object surface of the substrate or pattern where detail replication is required (such as, for example, edge definition is to be reproduced, and/or where
25 shadowing is to be avoided), and then subsequent modification of the spray parameters, (preferably as soon as possible after the said pattern detail and edge definition have been achieved), so as to spray relatively smaller droplets onto the object surface of the pattern or
30 substrate. (Preferably in order to bring stress control into operation, as described, for example, in WO-A-96/09421).

Alternatively, the process may comprise spraying of

relatively large droplets from one spray source onto the object surface of the substrate or pattern where detail is required (such as edge definition is to be reproduced, and/or shadowing effects are to be ameliorated), and
5 introducing a further spray of relatively smaller metallic droplets from a second spray source (preferably concurrently with the first spray), the further spray preferably being tailored to minimise internal stresses in the deposit.

10

It is preferred that the control step c) is operated by control means (preferably computer control means) and pre-programmed.

15

To achieve the required control, one or more spray guns are preferably mounted on manipulator means, such as an industrial robot which is preferably programmed, advantageously together with the spray guns, by the control means. Alternatively, or additionally, the one or
20 more sprays of metallic droplets generated by the spray guns may be scannable, in which case the means for scanning the sprays is preferably co-ordinated and controlled, preferably by the same control means.

25

The invention will now be further described, by way of example only, and with reference to the accompanying drawings in which:

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Figures 1(a) and 1(b) are explanatory sectional views of known spray deposition processes, highlighting the problem of shadowing and bridging known in the prior art.

Figure 2 is a schematic view of apparatus for

use in the process according to the invention.

Referring to Figure 1(a), there is shown a substrate 101 rotated beneath a pair of arc-sprayed metallic droplet sprays 103 and 104. The arc sprayed metallic droplets are sprayed from two arc spray guns mounted on a 6-axis industrial robot (not shown) to produce a sprayed footprint 102, which is moved over the substrate by the robot manipulating the guns together, to produce a deposit 105 re-producing the object surface 106 of the substrate 101. The surface topography of object surface 106 is such that it is provided with a channel 107 having a pair of parallel sides 107a, 107b and a perpendicular surface 107c. As the spray deposition continued, the sprayed deposit 105 builds up on the object surface 106 eventually bridges the width of channel 107 leaving a void 108, as shown in Figure 1(b) caused by the shadowing effect of the build up of deposit 105.

It has been found, surprisingly, that by initial spraying with droplets of larger size than used conventionally in spray deposition metallurgical techniques, the effects of shadowing and bridging, in situations where the surface topography of the object surface 106 is varied, are modified substantially. Furthermore, external and internal deposited edges (such as edges 105a to 105d) are formed with superior integrity than would otherwise be the case where droplets of conventional size are used. It has been found that sprays having droplets distributed about gaussian mean of 200 microns and above (preferably 350 microns and above) provide significant process advantages. It is believed that the use of larger droplets may provide enhanced process performance because one or either of the following occur:

(a) droplets have increased momentum and remain liquid longer with more opportunity for flow driven by the momentum;

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(b) "splashing" of particles on impingement with substrate or deposit lessens "line of sight" problems.

10 Using the apparatus shown in Figure 2 the improved performance of the process according to the invention can be achieved. The apparatus of Figure 2 comprises arc spray guns 1,2 mounted on a 6-axis industrial robot 10, producing atomised metal sprays 3,4 which impinge upon
15 pattern or substrate 5. Pattern or substrate 5 sits on a rotating table 6, and is provided with a varied topography object surface 7. A computer control arrangement 8 is used to control manipulation of the robot 10, and also co-ordinate and control process parameters of the respective
20 sprays 3,4 produced by guns 1,2 (such as, for example, the gas spraying pressure, and wire feed rate/current of the respective guns 1,2). The apparatus is completely enclosed within a dustproof acoustic chamber 9, connected to an appropriate dust and fume extraction system (not shown).

25

Example

Both spray guns 1,2 were used to spray low carbon steel (from stock feed wire). For the particular model of arc
30 spray guns used, an initial spray droplet size of approx. 350 microns could be achieved by means of propelling compressed gas at a pressure of 2.6 bar. These conditions were maintained for a period of approximately 120 seconds, for both spray guns. This length of time was sufficient to

ensure that all internal and external edges of the object surface of the substrate were covered by deposited spray having droplets of average diameter 350 microns approx. Spraying parameters for both arc spray guns were then
5 adjusted by increasing the pressure of the propelling gas to 3.5 bar and simultaneously decreasing the current supply in order to decrease the rate of generation of molten metal in the arc. These conditions were used to produce a finer droplet size below 150 microns for
10 building up the remainder of the deposit, and to control stresses according to WO-A-96/09421.

The deposit was subsequently released from the substrate 5 and found to have improved edge integrity and less
15 extensive shadowing or bridging defects than would have been the case when conventionally spraying with droplet sizes of less than 150 microns throughout the process.

Claims:

1. A process for producing a metallic tool, mould, die
or other body of significant thickness or a coating,
5 the process comprising directing a spray comprising
molten metallic droplets carried by a propelling gas
toward an object surface of a substrate or pattern so
as to build up a metallic deposit or coating
comprising the mould, tool, die, body or coating on
10 the object surface of the substrate or pattern,
wherein at one or more predetermined stages during
spraying droplets of a relatively large mean size are
sprayed and at one or more other stages droplets of a
relatively smaller mean size are sprayed.
15
2. A process according to claim 1, wherein the
relatively larger droplets are sprayed at a stage
preceding the spraying of relatively smaller
droplets.
20
3. A process according to claim 1 or claim 2, wherein a
metallic tool, mould, die or other body of
significant thickness is produced on a substrate or
pattern including topographical relief features, the
25 switching between spraying relatively larger and
smaller droplets being dependent upon the nature of
and/or the location of the topographical relief
features.
- 30 4. A process according to claim 3, wherein the
relatively larger droplets are sprayed onto the
topographical relief surface, the spray subsequently
being switched to spray the relatively smaller
droplets.

5. A process according to any preceding claim, wherein the droplets are produced by arc spraying.
- 5 6. A process according to any preceding claim, wherein when spraying droplets of the relatively smaller size, spray parameters are tailored to control internal stresses in the deposited metal.
- 10 7. A process according to claim 6, wherein the spray parameters are tailored to effect phase change or reaction in the deposited metal.
- 15 8. A process according to claim 8, wherein the spray parameters are tailored to effect martensitic phase change in the deposited metal.
- 20 9. A process according to any preceding claim, wherein at one stage in the deposition process substantially only droplets of relatively larger mean size are sprayed.
- 25 10. A process according to any preceding claim, comprising spraying of relatively large droplets from one spray source onto the object surface of the substrate or pattern and introducing a further spray of relatively smaller metallic droplets from a second spray source.
- 30 11. A process according to claim 10, wherein the further spray of relatively smaller metallic droplets is operated concurrently with the first spray.
12. A process according to any preceding claim, wherein a

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change between spraying of relatively larger and smaller droplet size sprays is operated by pre-programmed control means.

- 5 13. A process substantially as herein described with reference to the accompanying drawings.

AMENDED CLAIMS

[received by the International Bureau on 19 July 2000 (19.07.00);
original claims 1-12 amended; original claim 13 cancelled;(3 pages)]

1. A process for producing a metallic tool, mould, die
or other body of significant thickness or a
coating, the process comprising directing a spray
comprising molten metallic droplets carried by a
propelling gas toward an object surface of a
substrate or pattern so as to build up a metallic
deposit or coating comprising the mould, tool, die,
body or coating on the object surface of the
substrate or pattern, wherein at one or more
predetermined stages during spraying droplets of a
relatively large mean size are sprayed and at one
or more other stages droplets of a relatively
smaller mean size are sprayed.
2. A process according to claim 1, wherein the
relatively larger droplets are sprayed at a stage
preceding the spraying of relatively smaller
droplets.
3. A process according to claim 1 or claim 2, wherein
a metallic tool, mould, die or other body of
significant thickness is produced on a substrate or
pattern including topographical relief features,
the switching between spraying relatively larger
and smaller droplets being dependent upon the
nature of and/or the location of the topographical
relief features.
4. A process according to claim 3, wherein the
relatively larger droplets are sprayed onto the
topographical relief surface, the spray
subsequently being switched to spray the relatively
smaller droplets.

5. A process according to claim 1, wherein the droplets are produced by arc spraying.
- 5 6. A process according to claim 1, wherein when spraying droplets of the relatively smaller size, spray parameters are tailored to control internal stresses in the deposited metal.
- 10 7. A process according to claim 6, wherein the spray parameters are tailored to effect phase change or reaction in the deposited metal.
- 15 8. A process according to claim 8, wherein the spray parameters are tailored to effect martensitic phase change in the deposited metal.
- 20 9. A process according to claim 1, wherein at one stage in the deposition process substantially only droplets of relatively larger mean size are sprayed.
- 25 10. A process according to claim 1, further comprising spraying of relatively large droplets from one spray source onto the object surface of the substrate or pattern and introducing a further spray of relatively smaller metallic droplets from a second spray source.
- 30 11. A process according to claim 10, wherein the further spray of relatively smaller metallic droplets is operated concurrently with the first spray.

12. A process according to claim 1, wherein a change between spraying of relatively larger and smaller droplet size sprays is operated by pre-programmed control means.

STATEMENT UNDER ARTICLE 19

Claims 5, 6, 9, 10, and 12 have been amended to be in proper form. The amendments to the claims are fully supported by the specification and drawings filed in the International Application and the priority document.

Early Stages

Later Stages

FIG 1(a)

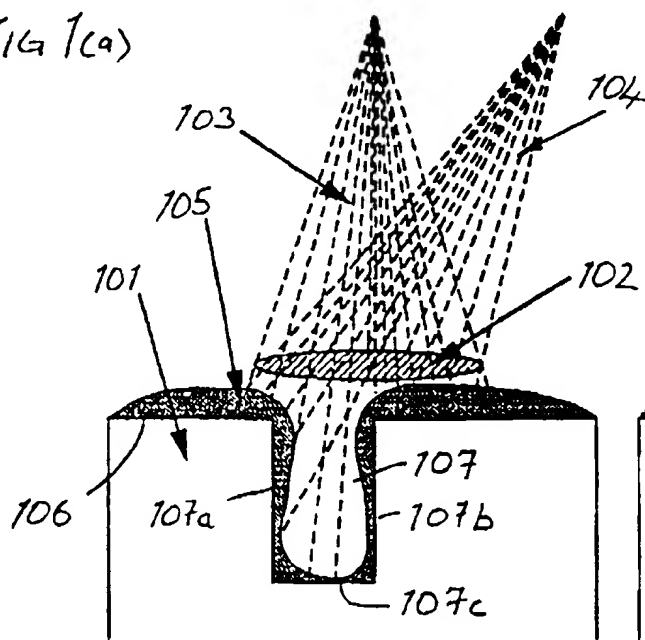


FIG 1(b)

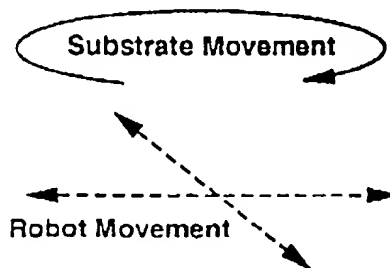
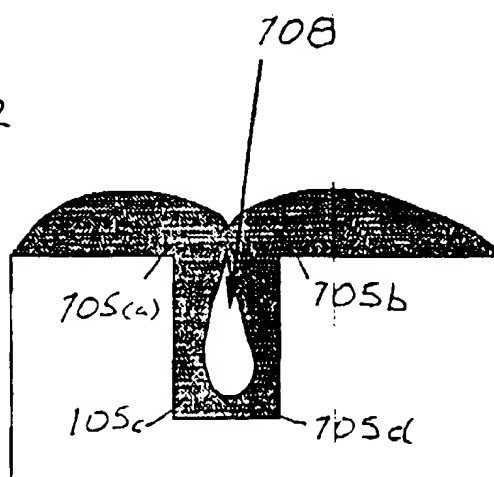
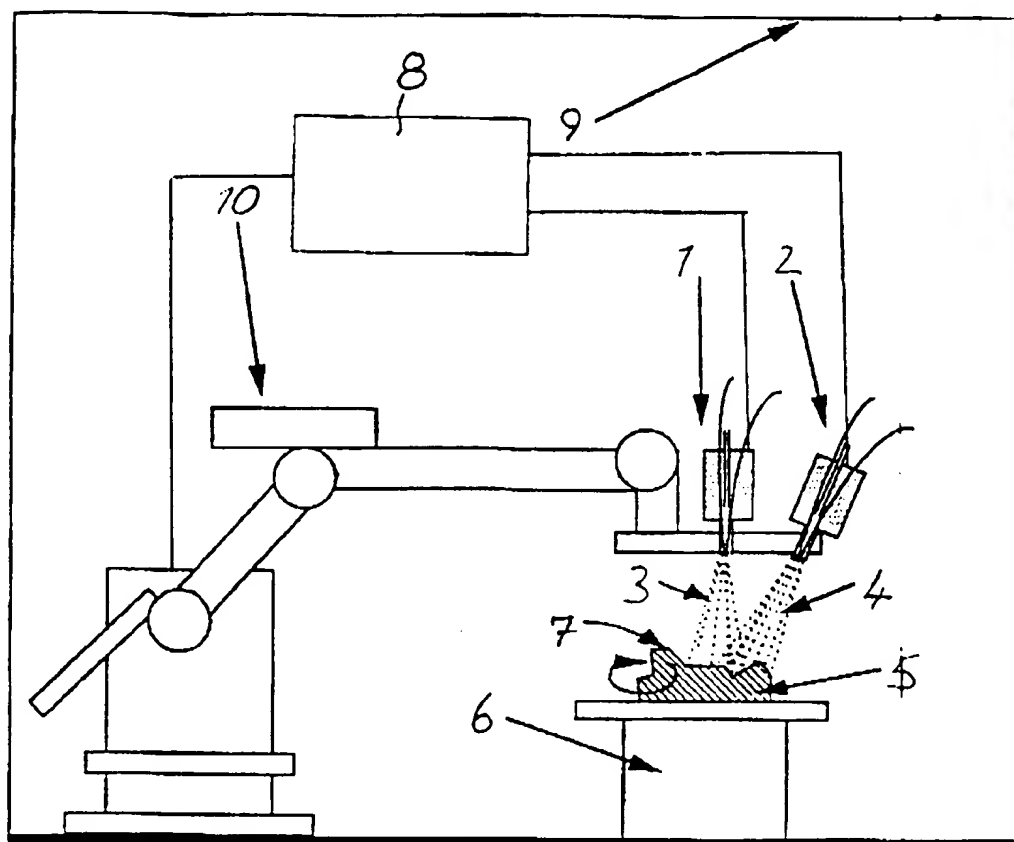


FIG 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/04494**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : B05D 1/08; B22D 23/00; C23C 4/08, 4/12

US CL : 164/46; 427/446, 455, 456, 422

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 164/46; 427/446, 455, 456, 422

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,817,267 A (COVINO et al) 06 October 1998, col.2, line 60 through col. 4, line 15 and col. 6, line 30 through col. 7, line 20.	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
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Date of the actual completion of the international search

05 MAY 2000

Date of mailing of the international search report

19 MAY 2000

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/04494

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 13
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

CLAIM 13 IS AN OMNIBUS CLAIM, AND FAILS TO POINT OUT WHAT IS INCLUDED OR EXCLUDED BY THE CLAIM LANGUAGE.

3. ☒ Claims Nos.: 5-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.